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A METHOD OF STUDYING TIME CHANGES IN INTENSITY OF SPECTRUM LINES RADIATED FROM SINGLE SPARKS

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A thesis submitted to the Department of Physics of the University of Alberta as a partial requirement for the degree of Master of Science.

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INTRODUCTION

The accuracy of spectrographic analyses is largely determined by the constancy of the relation between the relative intensities of spectrum lines radiated by the source and the amounts of the corresponding elements present in the sample. It is well known (3, 4, 6, 8, 13, 14) that even where the relative amounts of two elements in the sample remain constant, the intensity ratios of chosen line pairs arising from them may vary widely with changes in the amounts of other elements present. Langstroth and his co-workers have conducted investigations of the mechanisms operating in spark sources and the factors responsible for their variability in operation. They have shown the excitation to be predominantly thermal in character (11) and that changes in the transport phenomena accompany alteration of the general composition of a sample (12). Experiments involving additions of various substances to standard samples (14) revealed no obvious correlations between observed variations in intensity ratios and any of such factors as the excitation

potentials of the initial levels of the line pairs, the ionization potentials, atomic masses, or other physical properties of any of the elements involved. Addition to the samples of a large amount of a foreign substance (i.e. a buffer) does not always eliminate the variations, though in some instances it may minimize them (14).

In all of these studies the measurements made were for light gathered from a mumber of complete sparks, and often from several regions of the source. It has been pointed out (9, 14) that even for a single spark the observed intensities are summed values for many oscillatory discharges. Rotating-mirror photographs of single sparks (12) have shown that the radiation conditions change progressively over the successive discharges, and that these conditions differ from region to region in the source. Studies of the patterns left by single sparks on loaded plane electrodes (15) showed that the separate discharges may encounter widely differing conditions for the release of material from the electrode, the variability being

largely determined by the composition of the load. These studies indicate the desirability of obtaining information on the spectral intensities radiated from separate regions of single sparks during several intervals within their lifetimes. A technique allowing both time and space changes in the radiation to be followed for each wavelength would considerably enlarge the field of available information on spark source mechanisms.

This thesis is concerned with the development of a method for carrying out the studies proposed in the preceding paragraph and with a few preliminary results obtained thereby. The method involved the excitation of samples by a series of single sparks, and photography of the spectrum radiated, using a suitably controlled shutter of the electro-optical (Kerr Cell) type before the spectrograph slit. A sequence of exposures was taken, each identical with the others except that the shutter passed contributions of light from only the first "n" half-oscillations of each spark in the first exposure, the first 2n in the second exposure, and so on. The image

of the spark gap was focussed on the spectrograph slit so that the intensity variation along the length of a spectrum line had a point-to-point correspondence with intensity variation along the discharge axis. Spectrograms obtained in this way yielded information on the time changes in intensity at any point on the discharge axis for all wavelengths in the spectrum. Moreover the values obtained represented the mean behaviour for the number of sparks contributing to the exposure; the effects of unavoidable fluctuations in the source conditions were thus averaged out.

A few experiments of a very preliminary nature were carried out to determine the extent to which new information was made available by the method. Additions of boric acid were made to standard samples, both unbuffered and buffered with potassium acetate. The standard sample was composed of nickel, tin, and magnesium chlorides. Dilute solutions of each composition were loaded onto the plane electrode of copper point-plane pairs, and excited according to the procedure described.

The spectra obtained indicated that the intensities of spectrum lines change with time over the life of each single spark in a manner which depends upon the line studied and the general composition of the sample. The distribution of intensity along the discharge axis for any line also varies with time in a manner dependent on the sample composition. While portions of the data could be related in a general way to the mechanisms operating in the source, sufficient information for interpretation on this basis was not obtained. It is felt that the method provides a means for greatly extending the range of information available on the behaviour of spark sources.

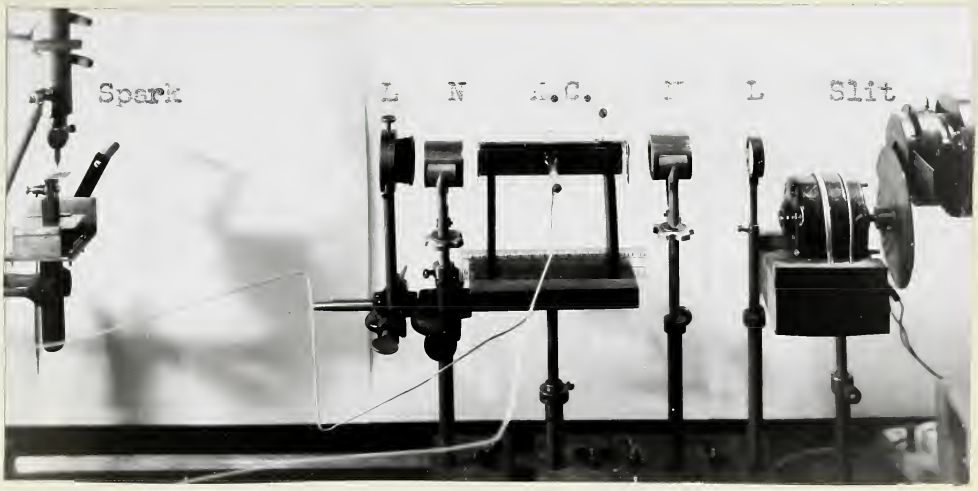
APPARATUS

To make possible the photography of the spectra radiated from selected portions of the life-times of single sparks, it was necessary to design an apparatus capable of controlled, reliable, and reproducible operation within times of the order of the period of oscillation of the sparks. This time is commonly 10^{-4} seconds or less. The succeeding paragraphs describe the essential features of an arrangement satisfying these requirements.

The Optical Shutter

The unsuitability of mechanical shutters at times of the order of 10^{-4} seconds led to the adoption of the electro-optical or Kerr Cell shutter (1, 2, 7). The cell, illustrated in Plate I, had a body constructed of Pyrex tubing, 12.5 cm. in length and 2.5 cm. internal diameter. The parallel-plate electrodes were of brass, 1/16 inch in thickness, 12.0 cm. long, and 2.0 cm. wide, with all edges smoothed and rounded. They were supported in position by thin brass rods

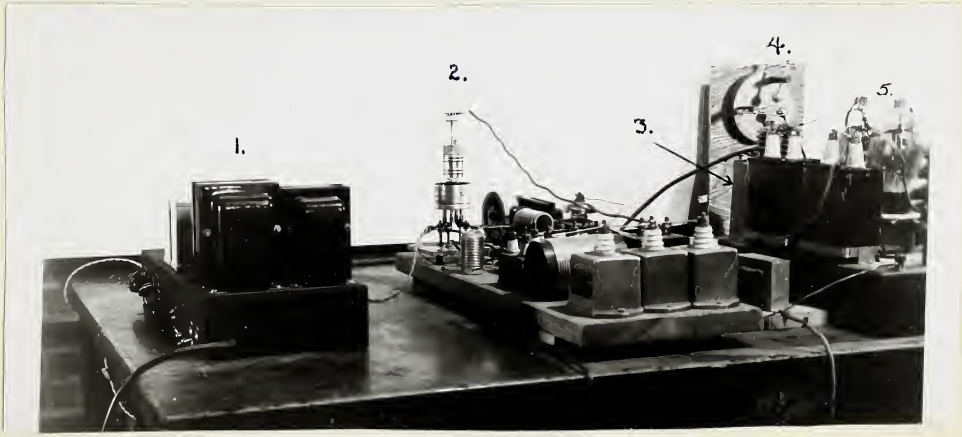
PLATE I



L, L Lenses N, N Foucault prisms K.C. Kerr Cell

The leads to the cell are from the spheres of the three-electrode gap shown in Plate II

PLATE II



1. Time-control circuits
2. Hydrogen thyratron
3. Pulse transformer
4. Three-electrode gap
5. Power Supply for Hydrogen Thyratron

extending out of the cell through sidearms to provide electrical terminals. A third sidearm was provided for filling the cell. When the plate separation had been adjusted to 0.5 cm. these rods were cemented into the sidearms with plugs of porcelain cement. The cell windows were thin plates of fused quartz selected for freedom from strain patterns, and affixed to the ends of the cell with a commercial china cement (Sheffield China Cement). The cements mentioned were chosen for resistance to the cell liquid (chloroform), and to minimize strain on the cell windows occasioned in setting. Both were unsatisfactory over long periods, tending to shrink and crack, occasioning leaks in the cell.

The cell was placed between crossed polarizers (Foucault prisms) whose optic axes were oriented at 45° to the electric field direction between the plates; this arrangement constitutes the optical shutter. The closing action of such shutters upon removal of the field is extremely rapid (7).

Neglecting absorption and reflection losses,

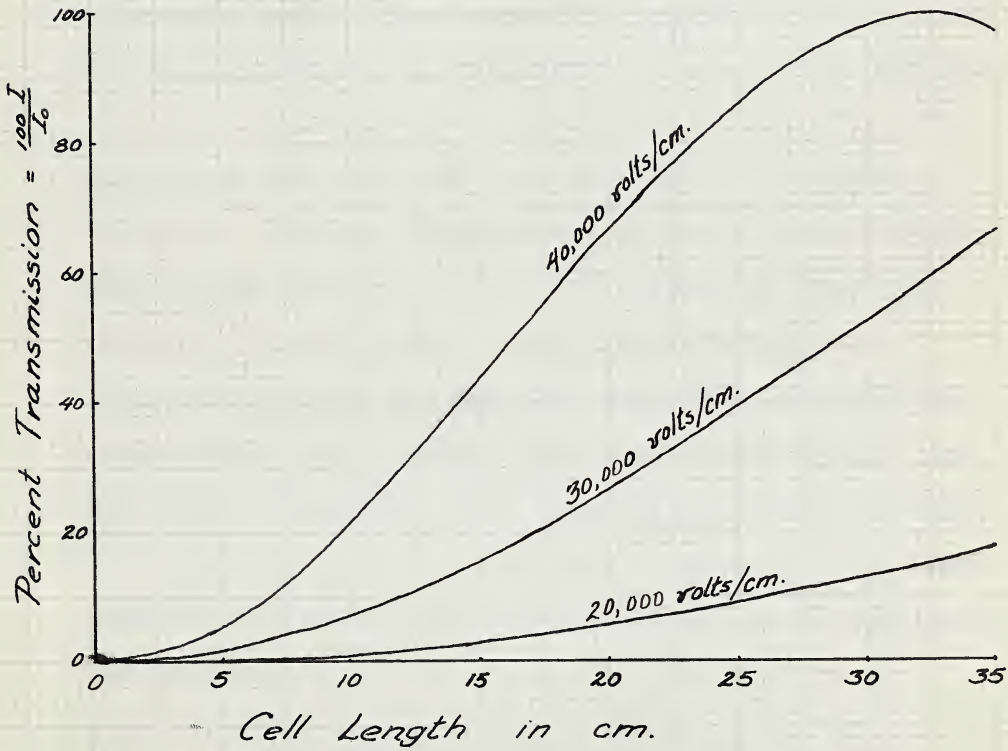
the intensity I passing the shutter when intensity I_o passes the first polarizer is given by

$$I = I_o \sin^2 (\pi b L E^2)$$

where E e.s.u./cm. is the applied field, L cm. is the 'effective' length of the plates, and b is the Kerr constant of the liquid used (10). It can be seen that high transmission is obtained with short cells and low field strengths only where a liquid of large Kerr constant is available. Nitrobenzene, with the largest known Kerr constant, is the most commonly used liquid in the visible wavelength region. The majority of the persistent lines used in analysis, however, lie in the region from 2,500 A to 4,000 A, where nitrobenzene is optically opaque (1, 10). A limited search for a cell liquid suitable for the present work led to the choice of chloroform. Graphs are presented in Figure 1 for the calculated transmission of chloroform shutters as determined by cell length and field strength. The Kerr constant used has been estimated at 3,000 A from data (18) on its variation with wavelength. It is obvious that high field strengths are necessary with this

FIGURE 1

Calculated Transmission of Chloroform Kerr Cells at 3,000 Angstroms, as a Function of Cell Length for Three Values of the Field Between the Plates



liquid, a condition which greatly restricts the design of the shutter closing mechanism. An operating voltage of 18 KV. was chosen, giving roughly 20% transmission for the cell used.

The conductivity of the cell must be kept extremely small, since convection currents will destroy the image quality; cleanliness in the cell and purity of the cell liquid are therefore important (7, 17). The electrodes were cleaned in nitric acid, thoroughly washed and dried. After assembly the cell was repeatedly filled with chloroform and allowed to stand for periods up to 48 hours. The chloroform used was of analytical grade, and was twice distilled in air, the middle half of the distillate being retained each time. The final filling was by a third distillation directly into the cell. The conductivity of this cell was quite appreciable, but no obvious distortion due to convection was present.

The voltage supply to the cell was from a resistance-capacitance filtered half-wave rectifier having a maximum output of 20,000 d.c. volts. A

glycerine resistor in series with the power supply allowed the cell to recharge completely within 3 to 4 seconds after each discharge. This procedure was enforced by the leakage, corona, and conductivity losses of the cell, which were sufficient to effectively close the shutter within six seconds after the cell had been charged and isolated. Some lowering of the voltage drop across the cell was thereby incurred.

For the present work, the shutter was required to remain open until light from the first "n" oscillatory discharges of the spark had passed, then close within a time short with respect to the period of oscillation, whichwas of the order of 10^{-4} sec. In view of other variations to be expected in the work, reproducibility to within about 2×10^{-5} sec. was considered sufficient. The operation to be performed under these time specifications was that of reducing the cell potential from 18 KV to something less than 5 KV, at which potential the shutter is effectively closed (7).

An extended search was carried out for a method of discharging the cell in the required manner.

Gas-filled (i.e. nitrogen, commercial neon) discharge tubes triggered into breakdown by high-frequency electrodeless discharge were shown to be suitable within a narrow range of pressures. The difficulties of constructing a stable model with the gases and equipment available caused this method to be discarded in favor of the arrangement illustrated by Figure 3.

A sphere gap (nickel-plated brass spheres of 2 cm. diameter) connected across the charged cell was triggered into breakdown by a high overvoltage pulse to a third electrode (nickel-plated brass point). This arrangement is reliable and free from appreciable time lags where overvoltages in excess of 100% are used for the trigger pulse, and where all electrodes are kept polished (5, 16). Preliminary oscillograph tests with low overvoltage indicated a time lag between the application of the trigger pulse and the discharge of the cell averaging less than 0.8×10^{-5} sec., never exceeding 2×10^{-5} sec. A condenser (.0007 μf) in parallel with the cell capacity and the sphere gap gave better reproducibility and completeness of discharge without detectible alteration in the discharging time.

Time Control and Associated Circuits

It was necessary to have the pulse which initiated the closing process occur at an accurately controlled interval after the breakdown of the light source gap. To this end the circuits illustrated in Figure 4 were employed.

On the breakdown of the light source spark, a tickler coil in the vicinity of the spark circuit inductance supplied a pulse to trip an 884 thyratron, whose function was to trigger the subsequent circuits, then shield them from the effects of further oscillations in the spark circuit. The breakdown of this thyratron initiated the action of a "one-shot oscillator". The operation of this circuit involved exchange of conduction current between two 6AC7 pentodes when an input pulse was received, and subsequent re-exchange at a time determined by the circuit constants R_T and C_T only. The increase of the anode potential of the second pentode on the re-exchange constitutes the output pulse, which, after suitable amplification, triggers the sphere gap across the cell.

Figure 2. The Spark Source Circuit.

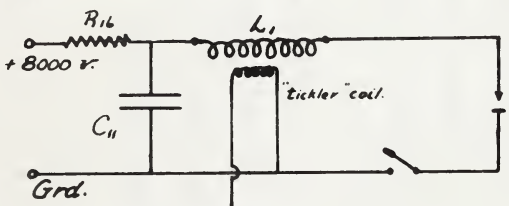
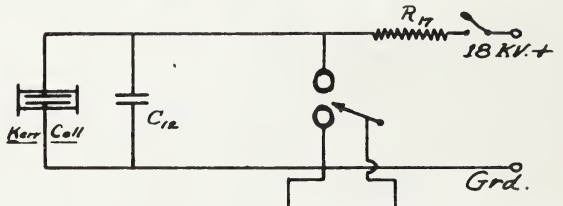


Figure 3. The Kerr Cell Circuit.



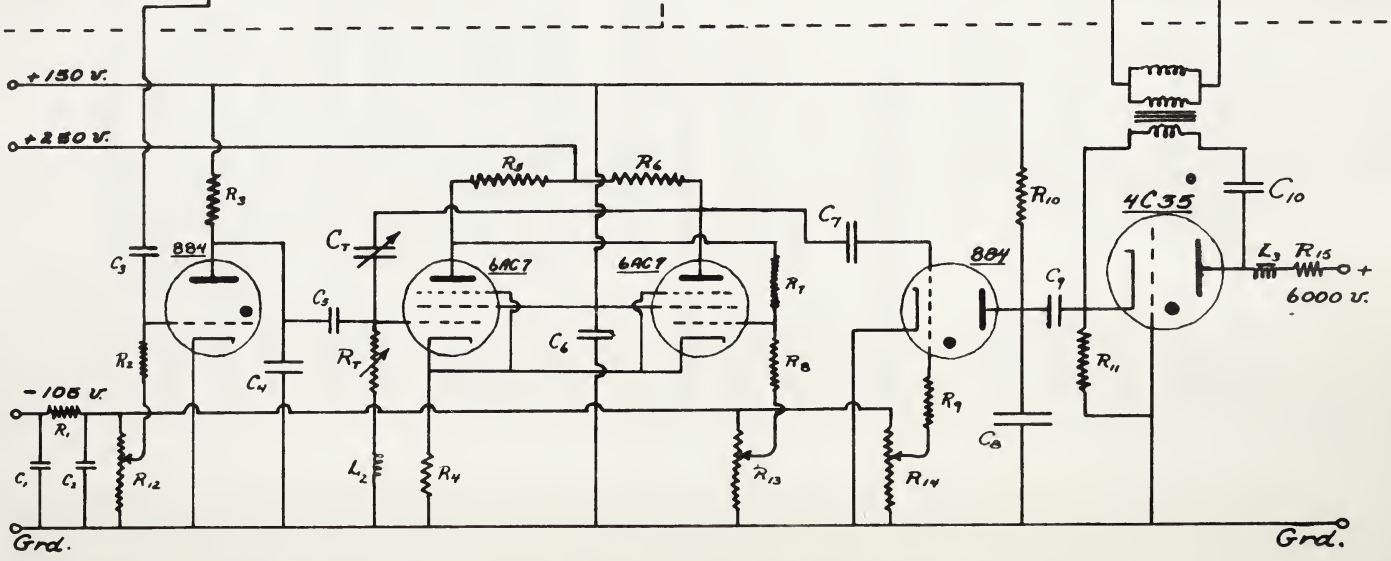


Figure 4. The Time Control and Pulse Amplifying Circuits.

The amplification involved an 884 thyratron stage which provided the energy to trip a 4C35 hydrogen pulse thyratron operated at zero grid bias and 6,000 volts plate potential. The energy released by the 4C35 breakdown fed the primary of a 1 to 4 ratio pulse transformer, whose secondary delivered a pulse in excess of 20,000 volts peak to the trigger electrode of the sphere gap. To minimize other operational time lags, the grids of all tubes were heavily overdriven.

Control of the time for which the shutter remained open consisted of selecting appropriate values of the time constant $R_\tau C_\tau$. The calibration of these values is described in a later section.

The Spark Source Unit

It was desirable that each spark contributing light to an exposure should take place under conditions identical with those for all other sparks in the series. At the same time, local irregularities in the electrode deposit should be averaged out by statistical sampling of the whole electrode area. For these reasons the

spark source unit was provided with a high series resistor and switch to control the passage of single sparks, and electrodes of the point and movable-plane type (13) permitted each spark to strike a fresh surface of the plane electrode.

The spark circuit (Figure 2) contained an 0.4 microfarad capacity, and an 0.35 millihenry inductance of negligible resistance. These values gave about 7.5×10^{-5} seconds as the estimated period of electrical oscillation. Oscillograph traces of the current wave confirmed this estimate, and indicated roughly linear damping, with an effective spark lifetime of about 16 half-periods.

The voltage was variable between zero and 10,000 d.c. volts, supplied from an inductance-capacitance filtered bridge rectifier of one kilowatt capacity.

Optical System and Spectrograph

The optical system and its relation to the cell discharge mechanism are shown in Plates I and II. All elements, including the spark stand were rigidly clamped

to an optical bench. The quartz-fluorite achromat L, (focal length 25 cm. speed f/5) sent light from the spark in a nearly parallel beam through the quartz Foucault prisms and the cell. The quartz lens L_2 (focal length 15 cm., speed f/5) focussed an image of the spark gap on the spectrograph slit. The rotating sector was used only for placing intensity calibration marks on each plate.

The spectrographwas a medium quartz instrument manufactured by Adam Hilger Ltd.

CALIBRATION

In the calibration of the time-control circuit, a rotating mirror was placed in front of the spectrograph, and a film holder was placed to one side to receive the reflected image of the spark gap. The speed of the mirror was adjusted to give resolution on the film of the light pulses emitted at each half oscillation of the spark. The low intensity passed by the shutter necessitated use of high speed (Eastman Tri-Pan) film, and reduction of the image magnification to about one-fifth. With a given adjustment of the circuit constants of the time-control network, thirty sparks were passed at random. On the average, three to four of these recorded themselves on the film. A series of exposures taken in this way enabled selection of the constants required to effect closing of the shutter after any desired number of half-periods. Plate III is a reproduction of an exposure obtained in this manner, showing transmission of light from 3, 6, and 9 half oscillations. The trace for the full spark is shown for comparison.

Several such exposures were taken for each setting, and in no instance was any variability detected in the closing of the shutter. Exposures taken with no time delay introduced except those delays inherent in the functioning of the various circuit elements showed closing of the shutter prior to the passage of any light recordable by the film. It can thus be stated that the lag in the closing process is of the order of a few microseconds at most.

PLATE III

Rotating mirror photographs of single sparks,
for calibration of time control network.

First row: Shutter closing after three half-periods.

Second row: " " " six " "

Third row: " " " nine " "

Bottom row: Shutter open for full spark lifetime.
The traces extend to the line marked "F".

EXPERIMENTAL

Samples Studied

The materials for study were chosen from those included in the work of Langstroth and Andrychuk (14) in case a comparison should prove desirable with data from studies in which the intensities were both time- and space-integrated over the whole of the spark. Table I lists the elements involved, their atomic masses and ionization potentials, the salt form in which each was originally introduced, the concentration of each salt in the sample solutions, and the mass of each salt per unit area loaded onto the electrodes. The last mentioned information is given on the assumption that the salt forms appearing on the electrode were those originally put into solution. This assumption is probably not true; the figures therefore indicate only relative amounts of each element present on the electrode. Information on the spectrum lines investigated is given in Table II.

Four solutions were prepared. Two consisted of the standard sample with no buffer, while two were buffered with potassium acetate. One solution of each type carried boric acid as an extraneous addition.

TABLE I: Composition of Samples

	Elements	Atomic Mass (mass units)	First Ion. Pot'l. (volts)	Salt Form Introduced	Salt Concentration in Solution (mgm./cc.)	Micrograms salt per cm^2 on electrode
Standard Sample	Ni	59	7.6	$NiCl_2.6H_2O$	1.00	44.5
	Sn	118	7.3	$SnCl_2.6H_2O$	0.94	41.7
	Mg	24	7.6	$MgCl_2.6H_2O$	1.05	46.7
Extraneous Addition	B	11	8.3	H_3BO_3	10.3	458.
Buffer Substance	K	39	4.3	Potassium Acetate	50.0	2220.

TABLE II: Spectrum Lines Investigated

Element	Wavelength (Angstroms)	Classification and Term Values ($cm.^{-1}$)	Ground Level ($cm.^{-1}$)	Excitation Potential (volts)
Sn	3262.33	$5p^2\ {}^1D_2 - 5p({}^2P_{3/2})6s\ {}^1P_1^\circ$ 50,579 - 19,935	59,192	4.86
Ni	3414.77	$3d^9 4s\ {}^3D_3 - 3d^9 4p\ {}^3F_4^\circ$ 204.8 - 29,480.9	0.0	3.66
	3566.37	$3d^9 4s\ {}^1D_2 - 3d^9 4p\ {}^1D_2^\circ$ 3,409.95 - 31,441.64	0.0	3.90

Wavelengths from M.I.T. Tables - Wiley, New York, 1929.

Energy levels from Bacher and Goudsmit - Atomic Energy States McGraw Hill, 1932.

Preparation of Electrodes

The solutions were loaded onto plane copper electrodes 1.5 cm. x 1.5 cm. with an 0.10 cc pipette calibrated to 2 percent. The electrodes were cleaned by dipping briefly in concentrated nitric acid, washing in running water, and rinsing in distilled water. The electrodes were loaded while a visible film of moisture still covered the surface, since this gave better deposition than where flame- or air-dried electrodes were used. The tendency of the salts to form a heavy outer ring on evaporation gave some difficulty. Small additions of gelatine yielded very uniform coatings, but their high dielectric strength rendered them unsuitable for sparking. Reasonably good deposits were obtained by intermittent evaporation under reduced pressure, the remaining liquid being redistributed over the whole electrode surface at each stage by gentle blowing through a pipette (14).

More electrodes of each kind were prepared than were needed, to allow a selection for uniformity of

deposit. Electrodes of the same loading were found to exhibit differences in the color and texture of the layer, even where the coatings appeared to have uniform thickness (see Plate IV).

Exposures

The spark gap was set at a separation of 4 mm. and its image formed on the spectrograph slit at a magnification of one-half. An auxiliary lens formed an image of the electrodes on a screen behind the spark, to facilitate their accurate replacement after each exposure. The spark was operated at minimum breakdown potential, as judged by the occurence of a detectible lag between the closing of the switch and the passage of the spark. Variability was noted in the lag for individual sparks on the same electrode, and in the breakdown potentials for electrodes of the same loading as well as for those of different loading.

The procedure for a single exposure was as follows. An electrode was placed in position and 300 single sparks were allowed to pass, with the shutter controls set to transmit light from the desired number of

half oscillations in each. The sparks were spaced at intervals of from four to five seconds to allow full re-opening of the shutter, and the plane electrode was moved horizontally so that each spark might strike a fresh surface of the deposit. The performance of the shutter on each spark was established by observation of the discharge gap across the cell. It was found that this gap failed to fire occasionally unless the electrodes were polished after every 150 sparks.

Sixteen such exposures were recorded on each of two Eastman 40 plates. The spectra radiated during the first three, six, and nine half-oscillations and during the complete spark were obtained for each of the four sample compositions. A slit width of 50 microns was used throughout. Each exposure for a given sample composition required a fresh plane electrode and a clean point; the results are therefore conditioned by the reproducibility of the electrode loading.

Intensity calibration marks were placed on each plate with a brass arc and step-sector. The arc was placed on the spectrograph axis 125 cm. from the slit,

and operated at 3.8 amps. with a 2 mm. electrode separation. An exposure of 3 seconds was taken with the sector turning at about 25 r.p.s.

Processing

Each plate was developed ten minutes in fresh D-61A developer, rinsed one minute in water, fixed thirty minutes in acid-harding fixer F-5, washed one hour in running water and dried. The temperature of all baths, including the wash, was kept within half a degree of 24° Centigrade.

Determination of Intensity

The intensities were determined by the standard method (19) using a microphotometer constructed at the University of Alberta.

As general precautions the microphotometer was allowed a twenty minute warm-up period, and zero and clear plate deflections were checked after every twelfth reading. The dimensions of the photometer beam in the plane of the plate were set to thirty-five microns width and 0.33 mm. length. This allowed each line to be

photometered at three places corresponding to regions of the gap just above the plane electrode, at the middle, and just below the point electrode. The photometered length at any place was closely one-sixth of the total length. Two readings were obtained for each of the three regions and the background of each line photometered.

Several calibration curves were obtained for each plate to cover wavelength range of the lines under investigation, since the slopes of these curves are in general different for different wavelengths. It was not necessary to know the relative intensities of the brass arc lines in terms of which the intensities of the investigated lines are given since only changes in intensity ratios were of interest in the study, and each plate carries a complete set of data.

Terminology

Interpretation of the data required consideration of the terms to be used in its description. Suppose that i_λ represents the instantaneous value at time t of the intensity radiated at wavelength λ. The photographic plate cannot record this value i_λ, but only the

total exposure in the time interval zero to t_1, which can be represented as

$$E_{(\lambda,t_1)} = \int_0^{t_1} i_\lambda \cdot dt, \text{ where in general } i_\lambda \text{ is a function of time.}$$

Comparison of exposures taken over the same time interval is equivalent to comparing the average intensities I_λ radiated over that interval as defined by

$$E_{(\lambda_1,t_1)} = I_{\lambda_1} \cdot t_1$$

$$E_{(\lambda_2,t_1)} = I_{\lambda_2} \cdot t_1 \quad \text{etc.}$$

The term "intensity ratio" as commonly used in spectrographic analysis refers to the quantity $I_{\lambda_1} / I_{\lambda_2}$ as just given. In the present work consideration has been given to intensities averaged over differing periods. Moreover, it has been necessary to refer to instantaneous as well as average values. The terms "intensity" and "intensity ratio" have therefore been restricted to apply to instantaneous values only. The quantities actually determined from the photographic plates are exposures in the sense defined above and have been referred to as such.

The term "exposure ratio" obviously has the significance $I_{\lambda_1}/I_{\lambda_2}$ wherever the ratio has been taken for two exposures of the same time duration, but not otherwise.

RESULTS

The results are presented graphically in Figures 5 to 8 inclusive. Each figure gives the complete data pertaining to a given sample composition. For all points the abscissa gives the number of half-periods for which each of three hundred sparks contributed light to the exposure.

The ordinates of the graphs designated (a), (b) and (c) on each figure are the exposures of the investigated lines expressed as percentages of arbitrary values. These arbitrary numbers for each line were chosen to minimize the average deviation between the results for a given sample composition from the two plates. This procedure was permissible since only exposure changes were of interest.

The ordinates of the graphs designated (d) to (l) inclusive in each figure are the exposure ratios of the line pairs, expressed as percentages of arbitrary values. These arbitrary numbers were chosen to minimize the average deviation between the results for the two

plates. This procedure was permissible since only changes in the ratios were of interest. It should be noted that the data for a given ratio remain directly comparable over all sample compositions; this is only approximately true for the line exposure data above.

FIGURE 5

Results For The Unbuffered Standard Sample With No Extraneous Addition.

A

Exposures of the individual lines plotted against exposure time in half-periods of the spark, for three regions of the source.

The symbol "F" refers to the full spark lifetime.

1. —— Sn 3262 2. —— Ni 3415 3. —— Ni 3566

B, C, D

Exposure ratios of the line pairs plotted against exposure time in half-periods of the spark, for three regions of the source.

The symbol "F" refers to the full spark lifetime.

Units

The units on the ordinate axes are in all cases arbitrary. See page 26.

Accuracy

The length of the "I" drawn through each curve represents the average deviation from the plotted values of the determinations from each of two plates.

Figure: 5 Standard Sample With No Addition
Unbuffered

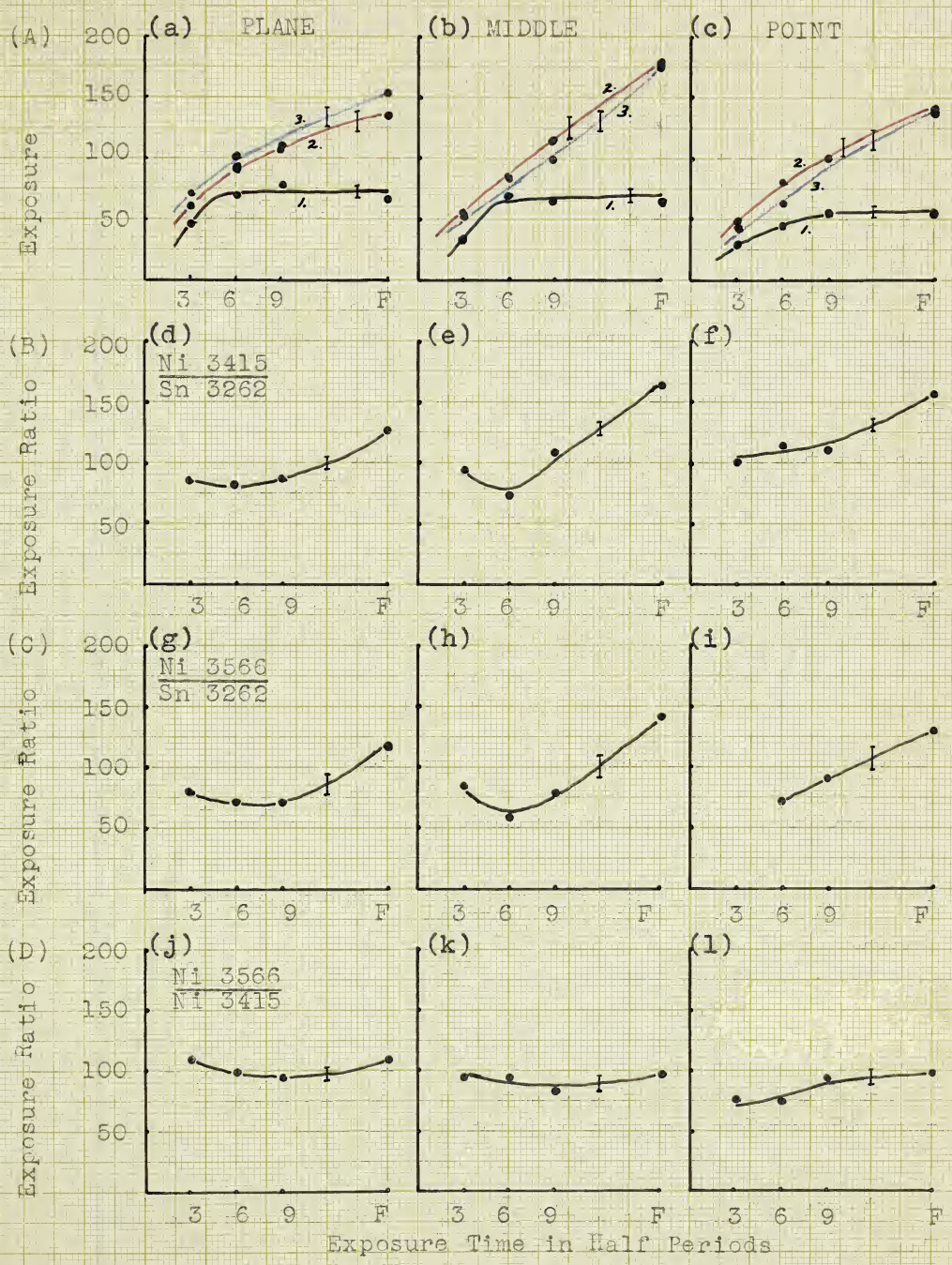


FIGURE 6

Results For The Unbuffered Standard Sample With Boric Acid Addition

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A

Exposures of the individual lines plotted against exposure time in half-periods of the spark, for three regions of the source.

The symbol "F" refers to the full spark lifetime.

1. —— Sn 3262 2. —— Ni 3415 3. —— Ni 3566

B, C, D

Exposure ratios of the line pairs plotted against exposure time in half-periods of the spark, for three regions of the source.

The symbol "F" refers to the full spark lifetime.

Units

The units on the ordinate axes are in all cases arbitrary. See page 26.

Accuracy

The length of the "I" drawn through each curve represents the average deviation from the plotted values of the determinations from each of two plates.

Figure: 6 Standard Sample With Boric Acid Addition
Unbuffered

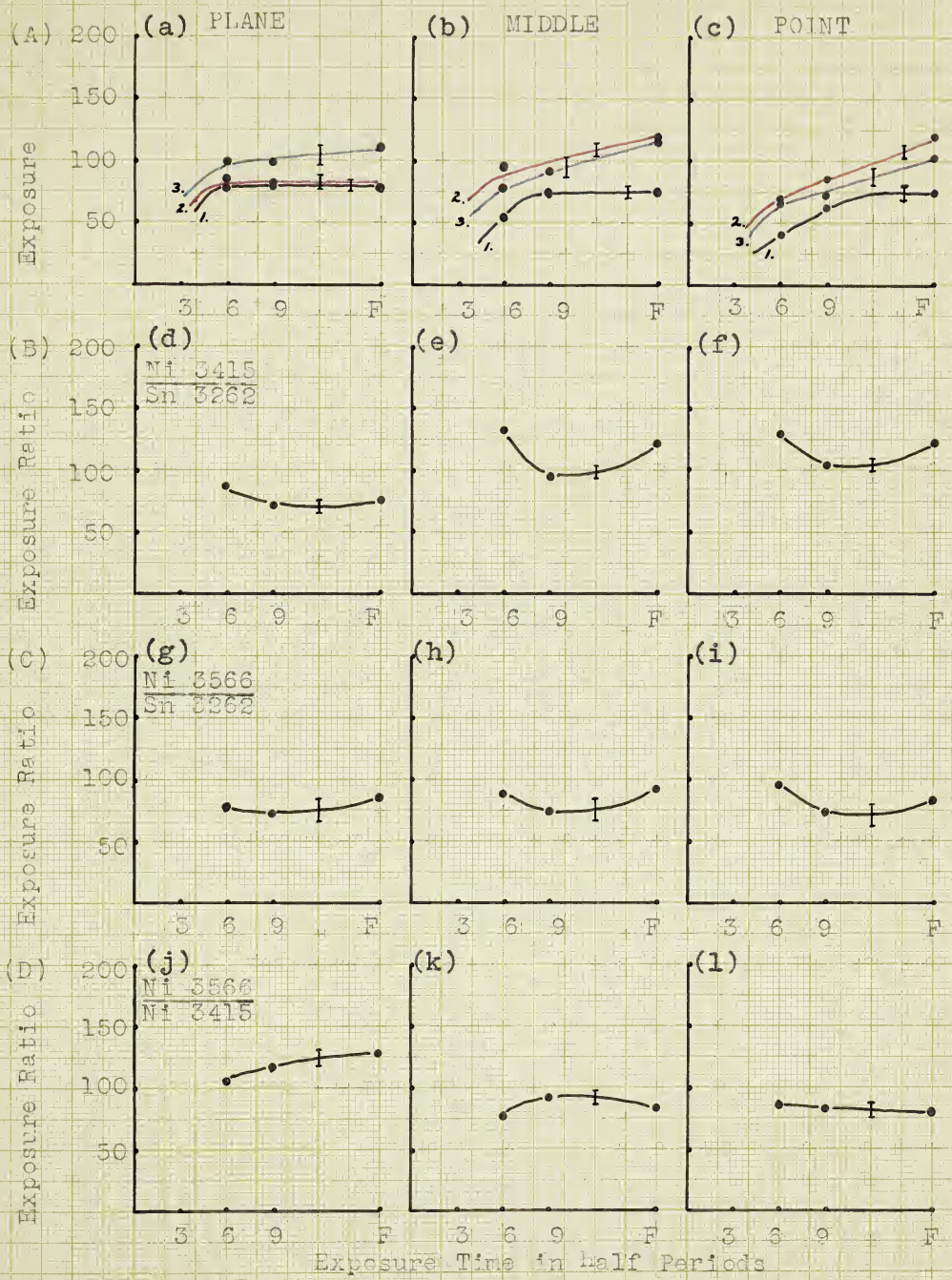

FIGURE 7

Results For The Buffered Standard Sample With No Extraneous Addition

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A

Exposures of the individual lines plotted against exposure time in half-periods of the spark, for three regions of the source.

The symbol "F" refers to the full spark lifetime.

1. —— Sn 3262 2. —— Ni 3415 3. —— Ni 3566

B, C, D

Exposure ratios of the line pairs plotted against exposure time in half-periods of the spark, for three regions of the source.

The symbol "F" refers to the full spark lifetime.

Units

The units on the ordinate axes are in all cases arbitrary. See page 26.

Accuracy

The length of the "I" drawn through each curve represents the average deviation from the plotted values of the determinations from each of two plates.

Figure: 7 Standard Sample With No Addition
Buffered With Potassium Acetate

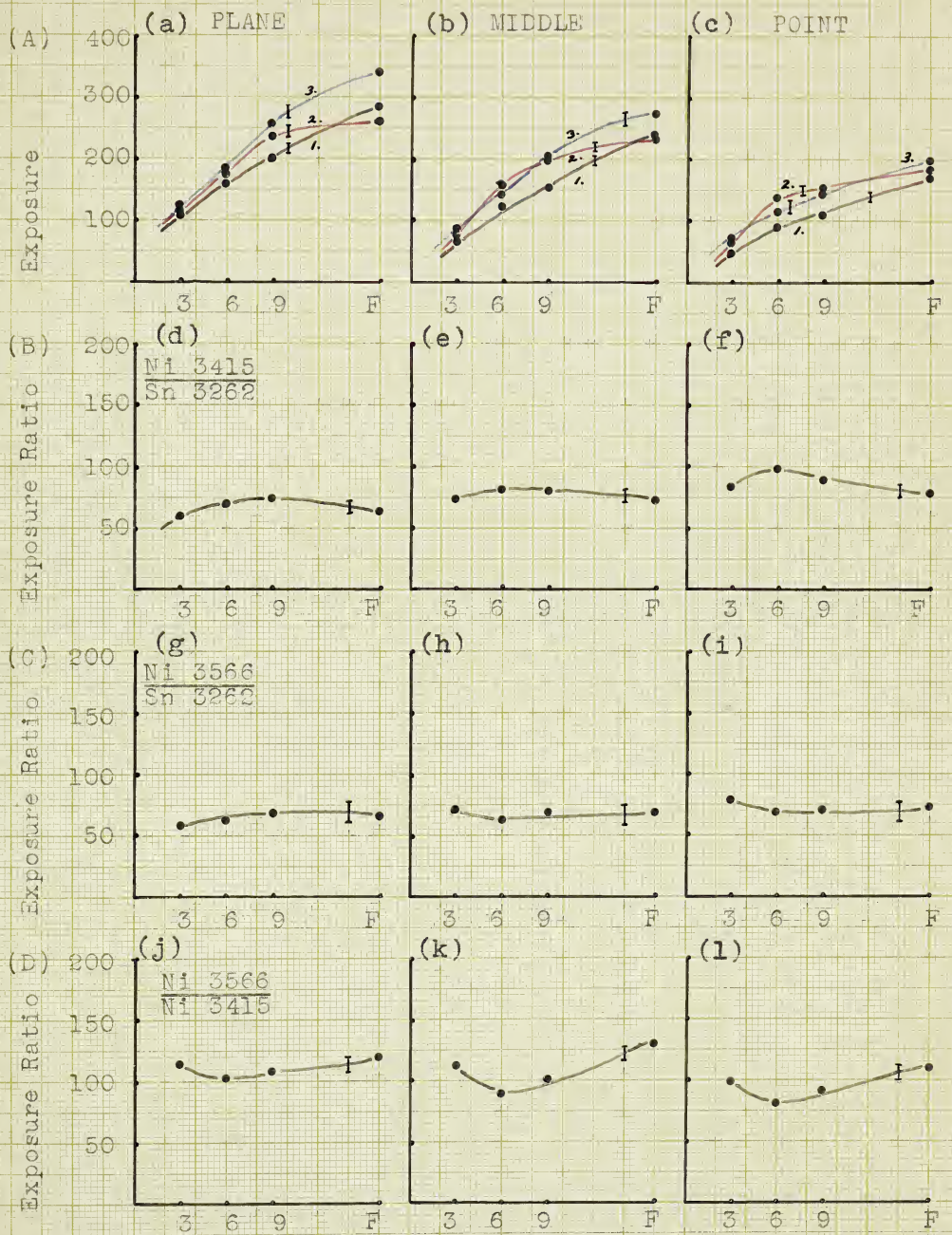

FIGURE 8

Results For The Buffered Standard Sample With Boric Acid Addition

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A

Exposures of the individual lines plotted against exposure time in half-periods of the spark, for three regions of the source.

The symbol "F" refers to the full spark lifetime.

1. —— Sn 3262 2. —— Ni 3415 3. —— Ni 3566

B, C, D

Exposure ratios of the line pairs plotted against exposure time in half-periods of the spark, for three regions of the source.

The symbol "F" refers to the full spark lifetime.

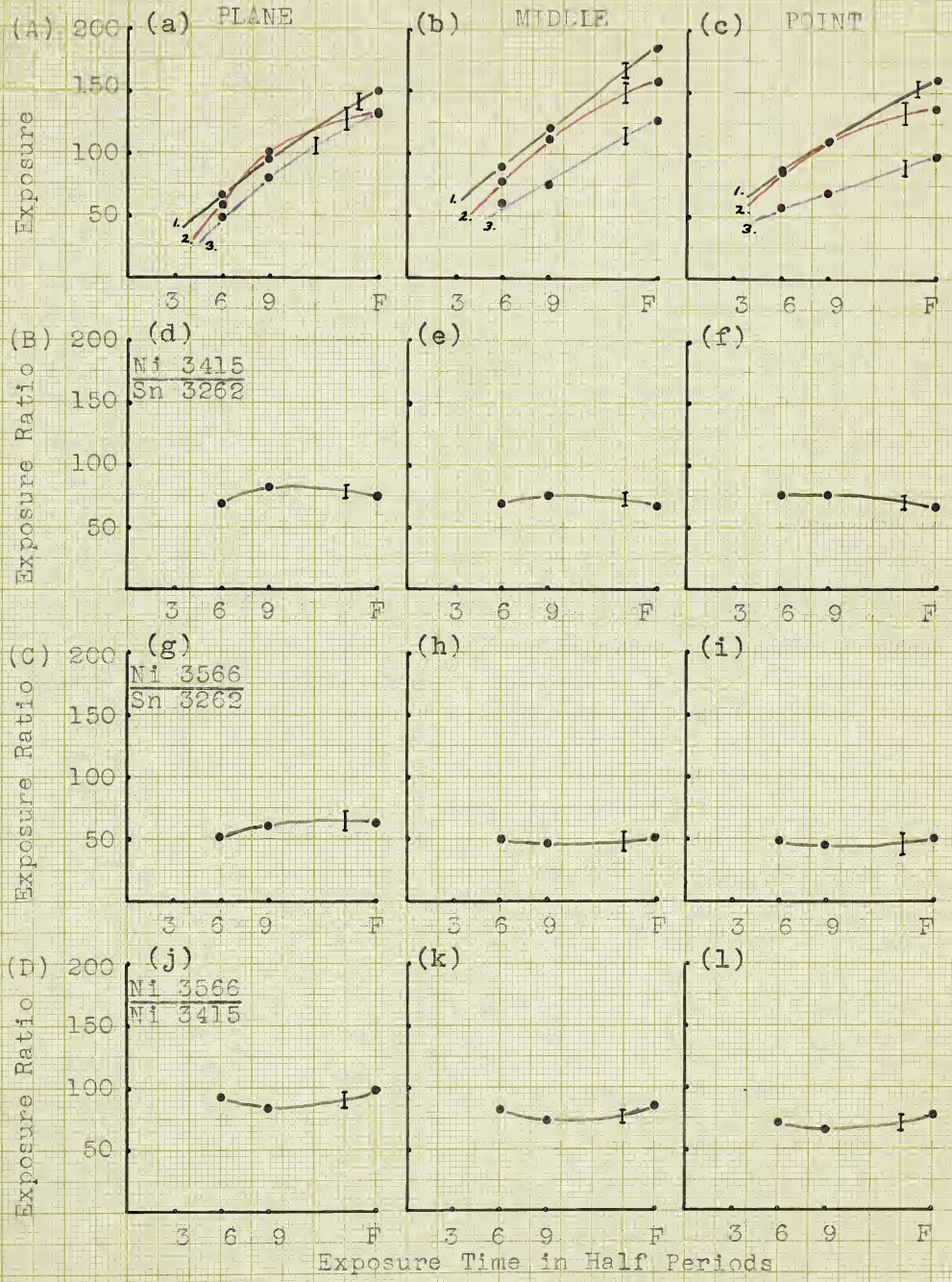
Units

The units on the ordinate axes are in all cases arbitrary. See page 26.

Accuracy

The length of the "I" drawn through each curve represents the average deviation from the plotted values of the determinations from each of two plates.

Figure: 8 Standard Sample With Boric Acid Addition Buffered With Potassium Acetate



DISCUSSION

Performance of the Apparatus

The evidence obtained in the calibration procedure (page 16) establishes the ability of the method to control the time for which single sparks may contribute light to an exposure. Specifically, the apparatus employed was free from unreliability where proper precautions (page 21) were observed, and gave sufficient reproducibility for the study of intervals as short as 10^{-5} seconds. In its present form, its use is restricted to the study of intervals which include the beginning of each spark. Electronic tubes are now available which permit the generation of square-wave pulses at amplitudes upwards of 12 kilovolts (20); the application of these tubes with a closed-to-open-to-closed shutter operation (1) would permit intervals to be selected for study from any desired portion of the spark lifetime. Adaptation to the study of the A.C. spark should offer few problems.

Interpretation of the Results - General Features

The results presented in the graphs of the previous section are of a very preliminary nature, serving only to indicate the type of information made available by the method, and to suggest promising areas for further investigation. The chief feature of the data concerns the ability to compare exposures resulting from complete spark processes with exposures in which these processes are in different stages of development. Since the time rate of change of exposure is the average intensity radiated over the interval, the slopes at any time of the curves in row A of Figures 5 to 8 inclusive should be proportional to the absolute intensities being radiated at that time, averaged over the three hundred sparks concerned. Thus observed changes in the exposure ratio of a line pair can be related to the changes in line intensities which gave rise to them. A second feature is the ability to contrast exposure distributions along the discharge axis at one stage of the spark with those existing at other stages, and to correlate these with the exposure ratios at various regions of the gap.

While it is felt that these features provide important avenues to information on source mechanisms no extended analysis of the present data from this viewpoint has been possible. The accuracy of the data was not sufficiently high to allow quantitative estimates of relative intensity to be made from the exposure curves. The determinations of exposures from the two plates taken deviated from their mean values by roughly 10% on the average; thus the least change in an exposure which was considered significant was 20%. While the exposure ratios are subject to errors from both lines, the average deviation was again just less than 10%. Thus 20% has been taken as the least significant change in an exposure ratio. Further limitation is placed on the interpretation on two accounts. One concerns contamination of the point electrode by material carried over from the plane by previous sparks in a series. The second arises from the observation (12) that the total radiation in any half-oscillation is generally greatest near the cathode; comparison of exposures involving odd and even numbers of half-oscillations may be influenced

by this effect. Both factors tend to prejudice the axial exposure distributions. Despite these limitations, the results clearly establish certain features of spark behaviour not previously open to investigation. These features are discussed in the paragraphs which follow.

Discussion of the Results

Marked differences were observed between the behaviour of individual lines over the time intervals studied. Moreover, changes in sample composition had important effects on this behaviour. For example, the two nickel lines in Figure 5-A developed steadily over the whole spark lifetime, indicating approximately constant intensities after the third half-period. The exposure ratio Ni 3566/Ni 3415 therefore showed no significant variation over the spark lifetime. In sharp contrast, the exposure ratios Ni 3415/Sn 3262 and Ni 3566/Sn 3262 showed definite increases at all regions of the gap at times later than the sixth half-period. These effects resulted from the failure of the Sn 3262 exposure to increase after this time. The major portion

of the tin radiation occurred, therefore, prior to the third half-oscillation. This and other cases to be noted suggest the desirability of extending the studies to earlier times. While it was not possible to assign this behaviour to the effect of any single source mechanism, the release of material from the electrode was most strongly suggested, in that tin atoms must have been almost absent from the discharge after the earliest times.

When boric acid was added to the standard sample, the behaviour of the tin line was not much altered, although Figure 6-A indicates that the disappearance of the tin line occurs at progressively later times at regions out from the plane. The nickel lines, however, were radically changed in behaviour, particularly in the region of the plane electrode. The radiation of all three lines in this region took place almost entirely prior to the sixth half-period. In consequence the ratios in Figure 5 (d), (g) and (j) remained sensibly unchanged after this time.

When the standard sample was buffered with potassium acetate, neither of the marked effects

described for unbuffered samples was observed. Irrespective of whether boric acid was (Figure 8) or was not (Figure 7) present, all lines were sustained throughout the spark lifetime, and none of the ratios showed any pronounced variation with time. This is obviously a desirable aspect from the standpoint of the choice of buffer substances.

Evidence was obtained that conditions in the source may change with time in such a way as to alter the relationship between lines arising from the same element. The spectra for the unbuffered sample (Figure 5) showed closely parallel development of both nickel lines. The addition of boric acid caused the ratio Ni 3566/Ni 3415 to be higher near the plane than near the point at all times (Figure 6-A). The ratio Ni 3566/Sn 3262 showed little change along the axis, while Ni 3415/Sn 3262 increased towards the point; thus the excitation conditions along the gap were more favorable to Ni 3415 near the plane than near the point, while Ni 3566 was sensibly constant along the axis at all times. The presence of the potassium acetate buffer largely eliminated this effect (Figure 8).

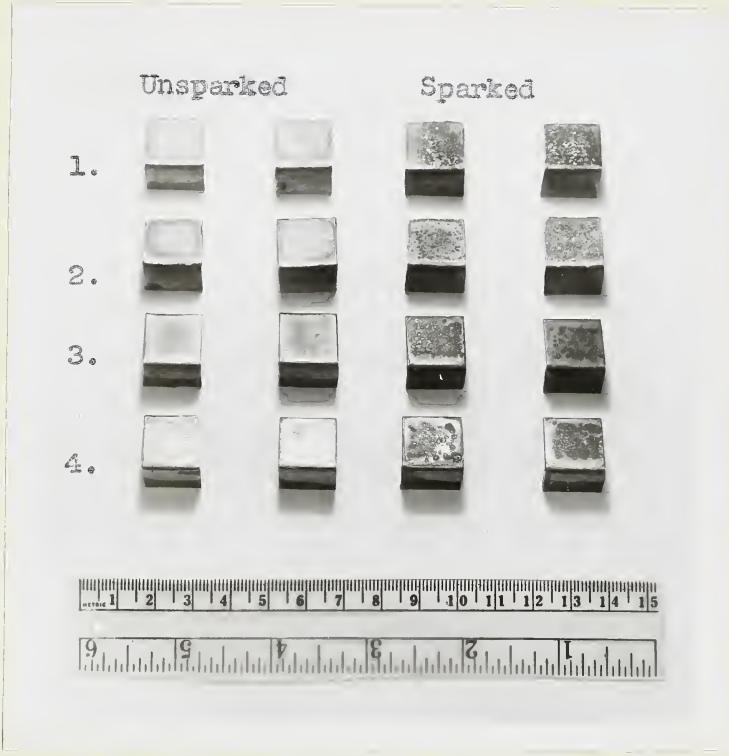
The exposure distribution of a line along the discharge axis was observed to shift with time under some conditions. For example, in Figure 5-A, the exposures of the nickel lines over the first three half-periods are highest near the plane. Over nine-half-periods the exposure distributions are uniform along the axis, while for the full spark the region of maximum exposure is near the centre of the gap. Corresponding shifts occur in the axial distribution of the exposure ratios. The presence of additions alters this behaviour. The buffered sample maintains the region of maximum exposure near the plane for all lines at all times. The addition of boric acid to the unbuffered sample leaves no clearly established trend for Ni 3566, while upward shifts near the point occur with increasing time for Ni 3415 and Sn 3262. The addition of boric acid to the buffered sample gave distributions initially higher near the point for all lines, the region of maximum exposure shifting towards the centre of the gap with increasing time.

The general levels of intensity were greatly altered by the additions. The intensities of all lines

in the spectrum, relative to those observed when the standard sample alone was sparked, were reduced by the addition of boric acid, and very greatly enhanced by the addition of the buffer. However, the weakest spectra were obtained when boric acid was added to the buffered sample. The cause of these alterations was not understood. It was noted on page 20 that the average minimum breakdown potential for a given electrode loading depended upon the composition of the load. The behaviour described above for the tin line Sn 3262 in unbuffered samples, and for the nickel lines in the unbuffered sample containing boric acid further indicated the importance of the release mechanism in spark sources. Additional evidence is given by the appearance of the electrode surfaces before and after sparking. Plate IV is a photograph of some of the electrodes used in this work, chosen to illustrate variability in the character of the electrode deposits, and differences in the action of the spark on the electrode surfaces. The observable differences between electrodes of the same load both before and after sparking emphasize an important cause of irreproducibility in experiments of this nature.

PLATE IV

Plane electrodes loaded with samples of varying composition, chosen to illustrate typical differences in the surfaces before sparking, and differences in the action of 300 sparks on the surfaces



1. Loaded with standard sample only.
2. Loaded with standard sample containing boric acid addition.
3. Loaded with buffered standard sample.
4. Loaded with buffered standard sample containing boric acid addition.

The more striking features concern the differences in sparking behaviour of different loads. For example, electrodes "buffered" with potassium acetate addition showed well defined "hot-spots" much fewer in number than the three hundred sparks which created them, while the electrodes carrying standard sample plus boric acid showed widely variable behaviour, the separate discharges within a single spark often striking to different spots on the electrode. These observations are notable only in that they call further attention to the role of the release mechanism in the source, and to the dependence of this mechanism on the character of the electrode surface.

Apart from these very general statements, no attempt was made to interpret the data in terms of source mechanisms. An extended program of experiments of higher accuracy is prerequisite to any such attempt. The comparison suggested on page 18 with the work of Langstroth and Andrychuk (loc. sit.) yielded no very significant conclusions. The average values of the full spark exposure ratios in this study are not comparable

to exposures integrated over the whole of the spark as in their work. However, general agreement was obtained for the order of size of the indicated changes in nickel-tin exposure ratios due to boric acid additions.

CONCLUSIONS

The following conclusions are presented on the basis of the work outlined in this report.

1. A method has been outlined for obtaining photographs of spectra radiated from known intervals within the lifetimes of single sparks, employing a shutter of the Kerr Cell type.

2. A first model of the working arrangement has been described. Where proper precautions are observed its reliability and reproducibility have been shown to be adequate for the study of sparks of periods as short as 10^{-5} seconds.

3. Intensities of spectrum lines radiated from any region of the source change with time over the life of each single spark. The manner in which changes occur depends upon the individual line studied and upon the composition of the sample excited.

4. The distribution of intensity along the discharge axis for any line may change with time over

the life of each single spark. The manner in which changes occur depends upon the individual line studied and upon the composition of the sample excited.

5. The intensity ratio of a line pair at any region of the source and its distribution along the discharge axis may vary over the spark lifetime in a manner dependent on the general sample composition, whether the lines arise from the same or from different elements.

6. While certain portions of the data could be related in a general way to such factors as release of material from the electrode and excitation conditions in the discharge, the information obtained was insufficient to permit any interpretation in terms of source mechanisms.

7. Extended experiments of higher accuracy are needed before the various source mechanisms can be effectively studied. It is felt that refinements in the method described will allow such studies to be accomplished.

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